原著論文

Copper-Catalyzed Monochalcogenation of Terminal Alkyne Using Dichalcogenide Compound via Cleavage of the Dichalcogenide Bond

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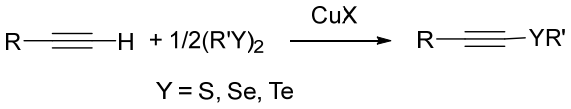

Abstract: The methodology for a copper-catalyzed chalcogenation of terminal alkynes with dichalcogenide in air. Numerous alkynyl sulfides, selenides or tellurides can be synthesized by the use of a CuCl catalyst and *N,N'*-dialkyl ethylenediamine. The employed diamine serves as a ligand of CuCl and a base facilitating the chalcogenation of alkynes. Furthermore, the present reaction can efficiently take advantage of two chalcogenide–groups in the dichalcogenide.

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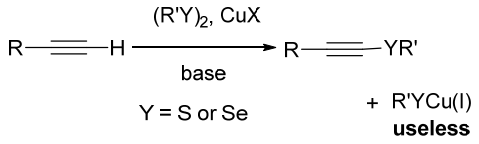
Introduction

Alkynyl chalcogenides have found widespread utilization as convenient intermediates in organic syntheses.[1,2] To furnish these compounds,[3] the reaction of terminal alkynes with dichalcogenide under basic conditions has often been employed,[3a,3b,4] whereas in the traditional system one chalocogenide-group in the dichalcogenide is not used.

The cause is attributable to the generation of anion.[5] Similarly, when the chalcogenation of alkyne using copper salt is carried out under basic conditions, copper(I) chalcogenide is produced together with alkynyl chalcogenide (Scheme 1). However, no copper-chalcogenide performs the chalcogenation of alkynes under usual conditions. Moreover, it is well known that the reactivity of this complex is lower owing to the stability of the metal-chalcogenide bond.[6,7] Therefore, an approach using a transition-metal-catalyzed method which can use two chalcogenide-groups has been limited.[8].

In this paper, a copper-catalyzed preparation of alkynyl chalcogenide from a terminal alkyne with dichalcogenide will be described.

Scheme 1. The chalcogenation of alkyne with dichalcogenide via copper-acetylide



Results and Discussion

Initial screening sulfidation of terminal alkyne was performed with copper(I) chloride as a catalyst (Table 1).

In air, when the phenylsulfidation of 1-octyne **1a** with diphenyl disulfide **2a** was executed using CuCl-bpy (10 mol%), 1-(phenylthio)-1-octyne was not detected at all (Table 1, entry 1). The employment of other diamines **7**, **8b** and **8c** or triethylamine **5** also did not produce satisfactory results owing to the dimerization of alkynes (Table 1, entries 2, 3, 4, and 5).

Fortunately, the combination of CuCl and *N,N'*-diethylethylenediamine **8a** (10 mol%) produced the corresponding sulfide **3aa** in 71% yield with the formation of diyne **4a** in 22% yield (Table 1, entry 6). Most notably, the reaction under nitrogen atmosphere using a balloon gave **3aa** in 90% yield, and

succeeded in suppressing the yield of **4a** (Table 1, entry 7).

A solvent such as DMF or toluene was unsuitable for the reaction (Table 1, entries 8 and 9). Although other copper catalysts were also examined, Cu^{I} salts (CuI, CuBr and CuOAc) gave lower yields (Table 1, entries 10, 11, and 12), and Cu^{II} salts ($CuCl_2$, $CuBr_2$ and CuF_2) could not advance the reaction (Table 1, entries 13, 14, and 15).

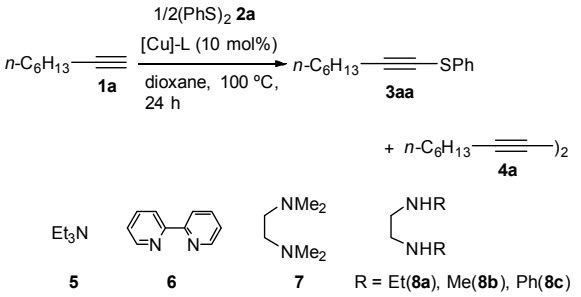
On the basis of the optimized result, we concurrently pursued the copper-catalyzed sulfidation and selenation of terminal alkynes using disulfide and diselenide (Table 2). When alkynes **1** (0.3 mmol), CuCl–**8a** or **8b** (10 mol%) and disulfides **2a**–**c** or diselenides **2d**–**e** were stirred in dioxane (0.5 mL) at 100 °C, alkynyl sulfides or selenides **3** were obtained in 60–94% yields. Regrettably, when (nBuS)$_2$ **2c** or propargyl amine was used, these yields decreased (Table 2, entries 3, 10 and 20). Thus this system could use the combination of miscellaneous alkynes with disulfides or diselenides.

Next, the synthesis of alkynyl tellurides was investigated. Unfortunately, employment of the previous conditions using the CuCl catalyst did not facilitate the telluridation owing to the dimerization of the alkyne (Table 3, entries 1, 2 and 3). To promote the expected reaction, the employment of other copper salts (CuBr, CuI, $CuCl_2$ or $CuBr_2$) was then examined, and, surprisingly, alkynyl telluride was produced in 47–60% yield (Table 3, entries 4, 5, 6 and 7). Furthermore, in the use of CuCl, the addition of nBu$_4$NBr led effectively to completion of the reaction and produced 1-(phenyltelluro)-1-octyne (**9af**) in 85% yield without the formation of diyne (Table 3, entry 9). According developed procedure, a variety of alkynyl phenyl tellurides **9** could be synthesized in 70–92% yields by the mixture of terminal alkyne, $(PhTe)_2$, CuCl–**8b** (5 mol%) and nBu$_4$NBr (20 mol%) treated in dioxane at 100 ºC (Table 4). In the present reaction, the production of **9** was not affected by the substrates.

Thus, the CuCl-catalyzed chalcogenation of terminal alkynes with dichalcogenides was achieved via cleavage of the dichalcogenide bond, and this system enabled the efficient use of two chalcogenide-groups in dichalcogenide.

Initially, to understand the reaction mechanism, the role of the copper catalyst was investigated in the case of sulfidation. The reaction of CuCl with diphenyl disulfide **2a** could not be promoted at all (Scheme 3), although the reaction of copper(I) phenylacetylide (0.3 mmol) with **2a** (0.15 mmol) produced the expected sulfide in 94% yield (Scheme 4). These results show that CuCl itself cannot cleave the disulfide bond, but the copper(I)-acetylide is formed in the first step of the catalytic cycle. Sequentially, both alkynyl sulfide and copper-sulfide were produced by the copper-acetylide reacting with disulfide.

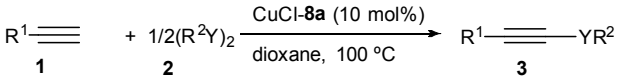
Table 1. Copper-catalyzed chalcogenation of 1-octyne with $(PhS)_2$



Entry	[Cu]	Ligand	**3aa**[c] (%)	**4a**[c] (%)
1[a]	CuCl	**6**	0	trace
2[a]		**5**	17	70
3[a]		**7**	29	41
4[a]		**8b**	30	42
5[a]		**8c**	trace	trace
6[a]		**8a**	71	22
7[b]		**8a**	90	trace
8[b,d]		**8a**	0	42
9[b,e]		**8a**	39	40
10[b]	CuI	**8a**	16	41
11[b]	CuBr	**8a**	60	23
12[b]	CuOAc	**8a**	7	trace
13[b]	$CuCl_2$	**8a**	trace	42
14[b]	$CuBr_2$	**8a**	trace	47
15[b]	CuF_2	**8a**	trace	trace

[a] Reaction was performed in air. [b] Reaction was performed under a nitrogen using the balloon. [c] Isolated yields after silica-gel chromatography. [d] DMF was used as a solvent. [e] $PhCH_3$ was used as a solvent.

Table 2. Copper-catalyzed preparation of alkynyl sulfides or selenides from terminal alkynes with dichalcogenide



$(PhS)_2$ **2a**, $(4\text{-}CH_3C_6H_4S)_2$ **2b**, $(n\text{BuS})_2$ **2c**, $(PhSe)_2$ **2d**, $(BnSe)_2$ **2e**

Entry	Y	**1**	Time (h)	**3**[a] (%)	Entry	Y	**1**	Time (h)	**3**[a] (%)
1	S	Ph—	24	94	12	S	*i*-Pr_3Si—	18	89
2	S	Ph—	24	86	13[b]	Se	Ph—	18	83
3	S	Ph—	48	53	14[b]	Se	Ph—	24	91
4	S	4-MeC_6H_4—	24	87	15[b]	Se	4-MeC_6H_4—	18	80
5	S	*n*-C_6H_{13}—	24	90	16[b]	Se	*n*-C_6H_{13}—	18	85
6	S	*n*-C_4H_9—	48	72	17[b]	Se	*n*-C_4H_9—	24	71
7	S	HO, Me	24	70	18[b]	Se	HO, Me	24	75
8	S	OH	48	91	19[b]	Se	OH	48	93
9	S	HO—	24	62	20[b]	Se	Me_2N—	24	62
10	S	Me_2N—	18	60	21[b]	Se		24	77
11	S		18	82	22[b]	Se	*i*-Pr_3Si—	18	88

[a] Isolated yields after silica-gel chromatography. [b] *N,N'*-Dimethyethylenediamine **7b** (10 mol%) was used as a ligand.

In fact, the reaction in the sealed tube (condition A) gave the corresponding sulfide **3aa** only in 11% yield in the presence of 10 mol% of CuCl, although the reaction under a nitrogen atmosphere using the balloon (condition B) resulted in 87% yield.[9] Accordingly, it is clear that oxygen has been supplied in the balloon from the atmosphere.[10]

Next, the role of the combination of $Cu^{I}SPh$ and diamine was surveyed (Table 5). The treatment of a mixture of CuSPh-**8b** (100 mol%) and 1-octyne **1a** gave **3aa** in 46% yield (Table 5, entry 1), and the use of CuSPh-**8b** (10 mol%) produced **3aa** in 81% yield by the addition of hydrochloric acid (10 mol%) (Table 5, entries 3 and 4).[11] Interestingly, the system in the absence of diamines **8b** rarely had the reaction promoted (Table 5, entries 2 and 5), although the reaction of sodium acetylide with CuSPh gave **3aa** in 38% yield (Scheme 6). From these results, it is presumed that CuSPh works for the phenylsulfidation of the terminal alkyne by **8b** serving as a base and a ligand.

The $Cu^{I}SPh$ produced herein is necessary for oxygen in order to facilitate the sulfidation of alkynes. In fact, the reaction in the sealed tube (condition A) gave the corresponding sulfide **3aa** only in 11% yield in the presence of 10 mol% of CuCl, although the reaction under a nitrogen atmosphere using the balloon (condition B) resulted in 87% yield.[10] Accordingly, it is clear that oxygen has been supplied in the balloon from the atmosphere.[11]

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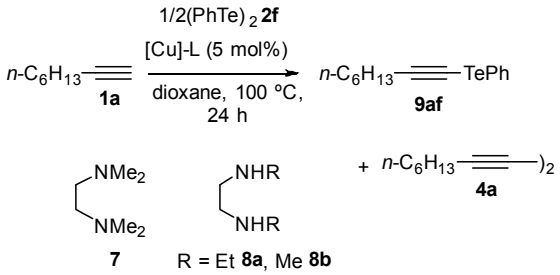
of the terminal alkyne by **8b** serving as a base and a ligand.

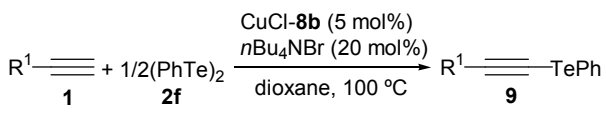
Table 3. Copper-catalyzed chalcogenation of 1-octyne **1a** with $(PhTe)_2$ **2f**[a]



Entry	[Cu]	Ligand	Additive	**3af**[b] (%)	**4a**[b] (%)
1	CuCl	**7**	none	0	92
2	CuCl	**8a**	none	trace	91
3	CuCl	**8b**	none	trace	95
4	CuBr	**8b**	none	50	trace
5	CuI	**8b**	none	47	trace
6	$CuCl_2$	**8b**	none	51	trace
7	$CuBr_2$	**8b**	none	60	trace
8	CuCl	**8b**	nBu$_4$NCl(20 mol%)	47	trace
9	CuCl	**8b**	nBu$_4$NBr(20 mol%)	85	0
10	CuI	**8b**	nBu$_4$NBr(20 mol%)	80	trace
11	CuBr	**8b**	nBu$_4$NBr(20 mol%)	76	0
12	none	none	nBu$_4$NBr(20 mol%)	32	0

[a] Reaction was carried out under a nitrogen using the balloon. [b] Isolated yields after silica-gel chromatography.

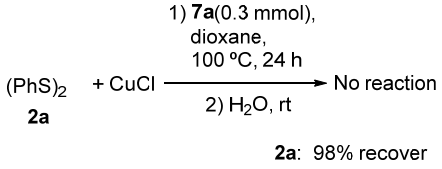
Table 4. Copper-catalyzed preparation of alkynyltellurides **9** from terminal alkynes with diphenyl ditelluride



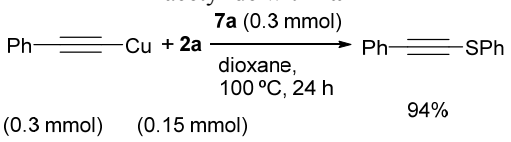
Entry	**1**	Time (h)	**9** (%)[a]
1	Ph—	24	82
2	4-MeC_6H_4—	24	92
3	n-C_6H_{13}—	24	85
4	HO, Me	24	87
5	OH	36	89
6	HO—	24	78
7	Me_2N—	24	70
8		24	81
9	i-Pr_3Si—	24	87
10	EtO_2C—	24	85

[a] Isolated yields after silica-gel chromatography.

Scheme 3. A reaction between $(PhS)_2$ with Cu(I)Cl

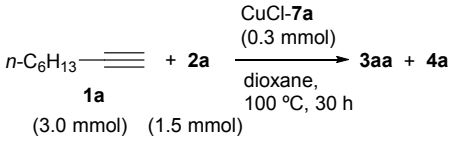


Scheme 4. A reaction between copper(I) phenyl acetylide with **2a**



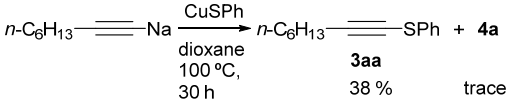
A proposed mechanism is outlined in Figure 1. In the first step, the reaction of copper-acetylide **10** with disulfide produces alkynyl sulfide **3** and $Cu^{I}SPh$ **11**. In the second step, a cuprate **12** as an intermediate is formed by the reaction of the generated **11** reacts with the terminal alkyne **1** in the presence of the diamines **8b**.[12] Finally, the alkynyl sulfide **3** is produced again by the oxidation of **12** and $Cu^{I}Cl$ is reproduced. Thus, this catalytic system can consume two chalcogenide-groups in the dichalcogenide.

Scheme 5. The large scale of sulfidation of **1a**



Condition	**3aa** (%)	**4a** (%)	**2a** (%)
A	11	8	71
B	87	trace	trace

A: in the sealed tube under N_2
B: under N_2 using the balloon

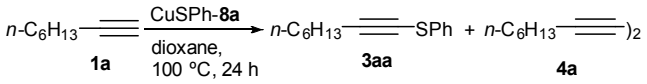


Conclusion

In conclusion, we have achieved a copper-catalyzed chalcogenation of a terminal alkyne with dichalcogenide under a nitrogen atmosphere using a balloon. The present reaction enables the efficient use of two chalcogenide-groups in the dichalcogenide by the diamines serving as a ligand and a base.

Scheme 6. A reaction of sodium acetylide with CuSPh

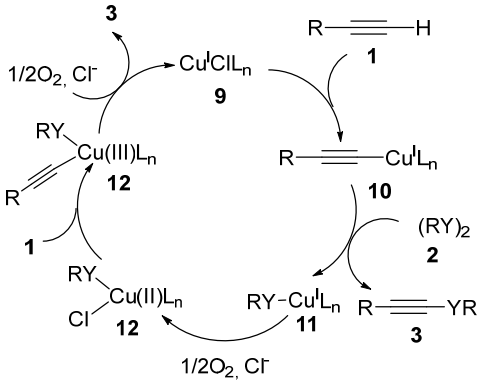
Table 5. Sulfidation of 1-octyne by Cu(I)SPh



Entry	Reagent (mol %)	CuSPh (mol %)	**8a** (mol %)	Additive (mol %)	**3aa**[a] (%)	**4a**[a] (%)
1[b]	none	100	100	none	46	20
2	none	100	none	none	5	trace
3	$(PhS)_2$(50)	10	10	none	5	12
4[c]	$(PhS)_2$(50)	10	10	HCl(10)	81	11
5	$(PhS)_2$(50)	10	none	HCl(10)	trace	trace

[a] Isolated yields after a silica-gel chromatography. [b] Reaction was carried out for 48 h in air.
[c] Hydrochloric acid used 37 wt.% in water.

Figure 1. A plausible reaction mechanism in the synthesis of alkynyl sulfide or selenide



Experimental Section

General. All reactions were carried out under a nitrogen atmosphere using the balloon. NMR spectra were recorded on a JEOL EX-270 spectrometer (270 MHz for ^{1}H, 67.5 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR and chloroform-*d* (δ 77.0) for ^{13}C NMR. IR spectra were measured by Perkin-Elmer Spectrum One FT-IR spectrometer. Melting points were measured on a BÜCHI Melting Point B-540 apparatus. Elemental analysis was performed at the Instrumental Analysis Center for Chemistry, Tohoku University (Japan).

Preparation of the alkynyl sulfides from terminal alkynes with disulfides

A typical procedure is given for the reaction of ethynylbenzene with diphenyl disulfide **2a** giving phenylethynyl phenyl sulfide (entry 1 in Table 2): To the mixture of Cu(I)Cl (3.0 mg, 0.03 mmol), diphenyl disulfide (32.8 mg, 0.15 mmol), and *N*,*N*'-diethylethylenediamine **8a** (3.5 mg, 0.03 mmol) in dioxane (0.5 mL), ethynylbenzene (30.6 mg, 0.3 mmol) were added under a nitrogen atmosphere using the balloon. The mixture was stirred at 100 °C for 24 h. After the solvent was cooled to room temperature, the reaction mixture was dissolved in Et_2O. The solution was washed with H_2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica gel

(Hexane) gave 1-phenyl-2-(phenylthio) etyne (59.1 mg, 94%) as a colorless oil.

1-Phenyl-2-(phenylthio) ethyne (Table 2, entry 1)[2b, 8a]: ^{1}H NMR ($CDCl_3$) δ 7.21 (t, *J* = 6.8 Hz, 1H), 7.31–7.36 (m, 5H), 7.45–7.52 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 75.5, 97.9, 122.9, 126.2, 126.5, 128.4, 128.6, 129.2, 131.7, 132.9; IR (neat) 2170, 1584, 1479 cm^{-1}; elemental analysis calcd for $C_{14}H_{10}S$ (210.30): C, 79.96; H, 4.79; found: C, 79.87; H, 4.82.

1-Phenyl-2-(4-tolylthio) ethyne (Table 2, entry 2): ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.29–7.39 (m, 5H), 7.45–7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.9, 76.1, 97.2, 123.0, 126.6, 128.3, 128.4, 128.6, 130.0, 131.6, 136.6; IR (neat) 2169, 1595, 1491 cm^{-1}; elemental analysis calcd for $C_{15}H_{12}S$ (224.32): C, 80.31; H, 5.39; found: C, 80.37; H, 5.34.

1-Phenyl-2-(butylthio) ethyne (Table 2, entry 3): ^{1}H NMR ($CDCl_3$) δ 0.96 (t, *J* = 7.4 Hz, 3H), 1.44–1.55 (m, 2H), 1.73–1.84 (m, 2H), 2.81 (t, *J* = 7.2 Hz, 2H), 7.25–7.30 (m, 3H), 7.39–7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.6, 21.4, 31.4, 35.5, 79.7, 92.8, 123.6, 127.9, 128.2, 131.4; IR (neat) 2930, 2959, 2166, 1595, 1486 cm^{-1}; elemental analysis calcd for $C_{12}H_{14}S$ (190.31): C, 75.74; H, 7.42; found: C, 75.61; H, 7.48.

1-(4-Tolyl)-2-(phenylthio) ethyne (Table 2, entry 4): ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.5, 74.4, 98.0, 126.1, 126.4, 127.5, 129.0, 129.1, 129.2, 131.8, 138.9; IR (neat) ν = 3058, 2167, 1582, 1507 cm^{-1}; elemental analysis calcd for $C_{15}H_{12}S$ (224.32): C, 80.31; H, 5.39; found: C, 80.39; H, 5.30.

1-(Phenylthio)-1-octyne (Table 2, entry 5)[2b,8a]: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 5.6 Hz, 3H), 1.26–1.38 (m, 4H), 1.41–1.48 (m, 2H), 1.53–1.63 (m, 2H), 2.44 (t, *J* = 7.1 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 7.9 and 7.6 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 20.3, 22.5, 28.5, 28.6, 31.3, 64.5, 100.1, 125.7, 126.0, 129.0, 133.8; IR (neat) 2930, 2857, 2193, 1583, 1478 cm^{-1}; elemental analysis calcd for $C_{14}H_{18}S$ (218.36): C, 77.01; H, 8.31; found: C, 77.09; H, 8.30.

1-(Phenylthio)-1-hexyne (Table 2, entry 6)[2d, 14]: ^{1}H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.42–1.51 (m, 2H), 1.53–1.62 (m, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 7.9 and 7.6 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5, 19.9, 22.0, 30.7, 64.5, 100.0, 125.7, 126.0, 129.0, 133.8; IR (neat) 2960, 2933, 2193, 1583, 1479 cm^{-1}; elemental analysis calcd for $C_{12}H_{14}S$ (190.31): C, 75.74; H, 7.42; found: C, 75.95; H, 7.53.

1-(Phenylthio)but-1-yn-3-ol (Table 2, entry 7)[2c]: ^{1}H NMR ($CDCl_3$) δ 1.55 (d, *J* = 6.6 Hz, 3H), 2.02 (br, 1H), 4.75 (q, *J* = 6.6 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.34 (dd, *J* = 7.9 and 7.2 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 24.2, 59.3, 71.5, 100.6, 126.3, 126.6, 129.2, 132.4; IR (neat) 3550, 2982, 2183, 1582, 1478 cm^{-1}; elemental analysis calcd for $C_{10}H_{10}OS$ (178.25): C, 67.38; H, 5.65; Found: C, 67.63; H, 5.77.

1-[(Phenylthio)ethynyl]-1-cyclohexanol (Table 2, entry 8)[2a]: ^{1}H NMR ($CDCl_3$) δ 1.26–1.31 (m, 1H), 1.51–1.76 (m, 7H), 1.97–2.03 (m, 2H), 2.13 (s, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.33 (dd, *J* = 7.9 and 7.2 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 23.2, 25.1, 39.8, 69.7, 70.6, 102.5, 125.9, 126.4, 129.2, 132.8; IR (neat) 3400, 2923, 2175, 1584 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{16}OS$ (232.34): C, 72.37; H, 6.94; found: C, 72.35; H, 6.94.

1-(Phenylthio)but-1-yn-4-ol (Table 2, entry 9)[8a]: ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 4H), 3.51 (s, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.9 and 7.2 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 44.1, 49.2, 70.8, 94.6, 126.1, 126.3, 129.1, 133.0; IR (neat) 3390, 2941, 2855, 1582, 1478, 1440 cm^{-1}; elemental analysis calcd for $C_{10}H_{10}OS$ (178.25): C, 67.38; H, 5.65; found: C, 67.49; H, 5.79.

1-(Phenylthio)-3-dimethylaminopropyne (Table 2, entry 10)[15]: ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 6H), 3.51 (s, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.9 and 7.2 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 44.1, 49.2, 70.8, 94.6, 126.1, 126.3, 129.1, 133.0; IR (neat) 2972, 2821, 2775, 2171, 1583, 1478, 1441 cm^{-1}; elemental analysis calcd for $C_{11}H_{13}NS$ (191.29): C, 69.07; H, 6.85; found: C, 68.80; H, 7.03.

1-[(Phenylthio)ethynyl] cyclohexene (Table 2, entry 11)[2a]: ^{1}H NMR ($CDCl_3$) δ 1.52–1.69 (m, 4H), 2.10–2.22 (m, 4H), 6.19–6.23 (m, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.31 (dd, *J* = 7.6 and 7.3 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4, 22.2, 25.7, 29.1, 71.9, 100.1, 120.7, 125.8, 126.2, 129.0, 129.1, 136.1; IR (neat) 2930, 2136, 1625, 1583, 1478 cm^{-1}; elemental analysis calcd for $C_{14}H_{14}S$ (214.33): C, 78.45; H, 6.58; found: C, 78.31; H, 6.59.

1-(Phenylthio)-2-(tri-isopropylsilyl) ethyne (Table 2, entry 12): ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 21H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.32 (dd, *J* = 7.9 and 7.3 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.4, 18.6, 91.1, 103.2, 126.0, 126.3, 129.1, 132.8; IR (neat) 2942, 2865, 2092, 1583, 1462 cm^{-1}; elemental analysis calcd for $C_{17}H_{26}SSi$ (290.54) C, 70.28; H, 9.02; found: C, 70.45; H, 8.90.

Preparation of the alkynyl selenides from terminal alkynes with disselenides

A typical procedure is given for the reaction of ethynylbenzene with diphenyl diselenide **2d** giving phenylethynyl phenyl selenide (entry 13 in Table 2): To the mixture of Cu(I)Cl (3.0 mg, 0.03 mmol), diphenyl diselenide (46.8 mg, 0.15 mmol), and *N*,*N*'-dimethylethylenediamine **8b** (2.6 mg, 0.03 mmol) in dioxane (0.5 mL), ethynylbenzene (30.6 mg, 0.3 mmol) were added under a nitrogen atmosphere using the balloon. The mixture was stirred at 100 °C for 18 h. After the solvent was cooled to room temperature, the reaction mixture was dissolved in Et_2O. The solution was washed with H_2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica

gel (Hexane) gave 1-phenyl-2-(phenylseleno) ethyne (64.0 mg, 83%) as a colorless oil.

1-Phenyl-2-(phenylseleno) ethyne (Table 2, entry 13)[8a]: ^{1}H NMR ($CDCl_3$) δ 7.23–7.35 (m, 6H), 7.48–7.51 (m, 2H), 7.57–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 69.2, 103.5, 123.2, 127.1, 128.3, 128.6, 128.9, 129.0, 129.5, 131.7; IR (neat) 3057, 2159, 1576, 1476 cm^{-1}; elemental analysis calcd for $C_{14}H_{10}Se$ (257.19): C, 65.38; H, 3.92; found: C, 65.40; H, 4.17.

1-Phenyl-2-(benzylseleno) ethyne (Table 2, entry 14): ^{1}H NMR ($CDCl_3$) δ 4.10 (s, 2H), 7.25–7.37 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 32.6, 33.0, 101.2, 123.5, 127.5, 128.1, 128.2, 128.6, 129.0, 131.4, 137.5; IR (neat) 3060, 3028, 2156, 1599, 1493 cm^{-1}; elemental analysis calcd for $C_{15}H_{12}Se$ (271.22): C, 66.43; H, 4.46; found: C, 66.15; H, 4.67.

1-(4-tolyl)-2-(phenylseleno) ethyne (Table 2, entry 15)[16]: m.p. 43.8-44.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.23–7.34 (m, 3H), 7.39 (d, *J* = 8.2 Hz, 2H) 7.57 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.5, 103.1, 120.1, 126.9, 128.9, 129.0, 129.1, 129.5, 131.5, 131.7, 138.8; IR ($CHCl_3$) 3017, 2159, 1577, 1567, 1477 cm^{-1}; elemental analysis calcd for $C_{15}H_{12}Se$ (271.22): C, 66.43; H, 4.46; found: C, 66.39; H, 4.59.

1-(Phenylseleno)-1-octyne (Table 2, entry 16)[8a]: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.25–1.38 (m, 4H), 1.40–1.48 (m, 2H), 1.52–1.64 (m, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 7.21–7.32 (m, 3H), 7.51 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 20.5, 22.5, 28.5, 28.6, 31.2, 57.3, 104.7, 126.6, 128.5, 129.3, 129.4; IR (neat) 2929, 2857, 1578, 1477 cm^{-1}; elemental analysis calcd for $C_{14}H_{18}Se$ (265.25): C, 63.39; H, 6.84; found: C, 63.56; H, 6.93.

1-(Benzylseleno)1-octyne (Table 2, entry 17): ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.24–1.39 (m, 6H), 1.40–1.53 (m, 2H), 2.32 (t, *J* = 6.9 Hz, 2H), 3.99 (s, 2H), 7.21–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.0, 20.4, 22.5, 28.5, 28.7, 31.3, 32.4, 58.9, 102.4, 127.3, 128.4, 128.9, 137.9; IR (neat) 2929, 2160, 1494, 1453 cm^{-1}; elemental analysis calcd for $C_{15}H_{20}Se$ (279.28): C, 64.51; H, 7.22; found: C, 64.21; H, 7.32.

1-(Phenylseleno)but-1-yn-3-ol (Table 2, entry 18): ^{1}H NMR ($CDCl_3$) δ 1.52 (d, *J* = 6.6 Hz, 3H), 2.08 (br, 1H), 4.72 (q, *J* = 6.6 Hz, 1H), 7.25–7.34 (m, 3H), 7.51 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 24.3, 59.4, 64.4, 105.5, 127.2, 128.3, 129.1, 129.5; IR (neat) 3369, 3057, 2940, 2180, 1577, 1476 cm^{-1}; elemental analysis calcd for $C_{10}H_{10}OSe$ (225.15): C, 53.35; H, 4.48; found: C, 53.07; H, 4.45.

1-[(Phenylseleno)ethynyl]-1-cyclohexenol (Table 2, entry 19): ^{1}H NMR ($CDCl_3$) δ 1.25–1.31 (m, 1H), 1.53–1.76 (m, 7H), 1.97–2.01 (m, 2H), 2.14 (s, 1H), 7.21–2.34 (m, 3H), 7.51 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 23.2, 25.1, 39.9, 63.8, 69.8, 107.5, 126.9, 128.7, 128.8, 129.5; IR (neat) 3377, 2935, 2166, 1577, 1477 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{16}OSe$ (279.24): C, 60.22; H, 5.78; found: C, 60.24; H, 5.89.

1-(Phenylseleno)-3-dimethylaminopropyne (Table 2, entry 20): ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 6H), 3.50 (s, 2H), 7.24–7.33 (m, 3H), 7.53 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 44.1, 49.4, 63.7, 99.1, 126.9, 128.8, 128.9, 129.4; IR (neat) ν = 2939, 2773, 2775, 1577, 1476 cm^{-1}; elemental analysis calcd for $C_{11}H_{13}NSe$ (238.19): C, 55.47; H, 5.50; found: C, 55.30; H, 5.64.

1-[(Phenylseleno)ethynyl] cyclohexene (Table 2, Entry 21)[3c,3i]: ^{1}H NMR ($CDCl_3$) δ 1.56–1.69 (m, 4H), 2.10–2.22 (m, 4H), 6.17–6.20 (m, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.30 (dd, *J* = 8.2 and 7.9 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4, 22.2, 25.7, 29.1, 65.4, 105.1, 120.9, 126.8, 128.6, 129.1, 129.4, 135.9; IR (neat) 2929, 2147, 1577, 1475 cm^{-1}; elemental analysis calcd for $C_{14}H_{14}Se$ (261.23): C, 64.37; H, 5.40; found: C, 64.29; H, 5.51.

1-(Phenylseleno)-2-(tri-isopropylsilyl) ethyne (Table 2, entry 22): ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 21H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.29 (dd, *J* = 7.9 and 7.2 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.4, 18.6, 85.1, 108.3, 126.8, 128.6, 128.9, 129.4; IR (neat) 2942, 2865, 2087, 1578, 1477, 1461 cm^{-1}; elemental analysis calcd for $C_{17}H_{26}SeSi$ (337.44): C, 60.51; H, 7.77; found: C, 60.56; H, 7.71.

Preparation of the alkynyl tellurides from terminal alkynes with ditellurides

A typical procedure is given for the reaction of ethynylbenzene with diphenyl ditelluride **2f** giving phenylethynyl phenyl telluride (entry 1 in Table 4): To the mixture of Cu(I)Cl (1.5 mg, 0.015 mmol), diphenyl ditelluride (61.4 mg, 0.15 mmol), *n*Bu_4NBr (19.3 mg, 0.06 mmol) and *N*,*N*'-dimethylethylenediamine **8b** (2.6 mg, 0.03 mmol) in dioxane (0.5 mL), ethynylbenzene (30.6 mg, 0.3 mmol) were added under a nitrogen atmosphere using the balloon. The mixture was stirred at 100 °C for 24 h. After the solvent was cooled to room temperature, the reaction mixture was dissolved in Et_2O. The solution was washed with H_2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica gel (Hexane) gave 1-phenyl-2-(phenyltelluro) ethyne (75.2 mg, 82%) as a pale yellow oil.

1-Phenyl-2-(phenyltelluro) ethyne (Table 4, entry 1)[8a,13]: ^{1}H NMR ($CDCl_3$) δ 7.24–7.34 (m, 6H), 7.44–7.48 (m, 2H), 7.73–7.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 47.2, 113.1, 114.2, 123.3, 127.9, 128.2, 128.6, 129.7, 131.9, 135.1; IR (neat) 2140, 1574, 1487 cm^{-1}; elemental analysis calcd for $C_{14}H_{10}Te$ (305.83): C, 54.98; H, 3.30; found: C, 54.94; H, 3.21.

1-(4-Tolyl)-2-(phenyltelluro) ethyne (Table 4, entry 2)[13]: m.p. 73.6–74.0 ºC; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.26–7.28 (m, 3H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.70–7.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4, 46.1, 113.2, 114.4, 120.3, 127.8, 129.7, 131.8, 134.7, 134.9, 138.8; IR ($CHCl_3$) 3019, 1574, 1507 cm^{-1}; elemental analysis calcd for $C_{15}H_{12}Te$ (319.86): C, 56.33; H, 3.78; found: C, 56.22; H, 3.93.

1-(Phenyltelluro)-1-octyne (Table 4, entry 3)[8a]: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.26–1.31 (m,

4H), 1.35–1.45 (m, 2H), 1.51–1.59 (m, 2H), 2.56 (t, J = 6.9 Hz, 2H), 7.20–7.26 (m, 3H), 7.64–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 21.1, 22.5, 28.5, 28.8, 31.2, 34.6, 113.1, 116.1, 127.5, 129.5, 134.6; IR (neat) 2928, 2856, 2158, 1574, 1474 cm^{-1}; elemental analysis calcd for $C_{14}H_{18}Te$ (313.89): C, 53.57; H, 5.78; found: C, 53.58; H, 5.88.

1-(Phenyltelluro)but-1-yn-3-ol (Table 4, entry 4): ^{1}H NMR ($CDCl_3$) δ 1.50 (d, J = 6.6 Hz, 3H), 2.04 (br, 1H), 4.75 (q, J = 6.6 Hz, 1H), 7.21–7.31 (m, 3H), 7.66–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.3, 42.2, 59.5, 112.3, 116.8, 128.0, 129.7, 135.3; IR (neat) 3369, 2155, 1572, 1474 cm^{-1}; elemental analysis calcd for $C_{10}H_{10}OTe$ (273.79): C, 43.87; H, 3.68; found: C, 43.92; H, 3.84.

1-[(Phenyltelluro)ethynyl]-1-cyclohexanol (Table 4, entry 5): ^{1}H NMR ($CDCl_3$) δ 1.24–1.28 (m, 1H), 1.51–1.73 (m, 7H), 1.90–1.98 (m, 2H), 2.15 (s, 1H), 7.23–7.27 (m, 3H), 7.64–7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 23.2, 25.1, 39.9, 69.9, 112.8, 116.9, 118.9, 127.7, 129.6, 134.7; IR (neat) ν = 3390, 2931, 2149, 1574 cm^{-1}; elemental analysis calcd for $C_{14}H_{16}OTe$ (327.88): C, 51.28; H, 4.92; found: C, 51.31; H, 5.08.

1-(Phenyltelluro)but-1-yn-4-ol (Table 4, entry 6): ^{1}H NMR ($CDCl_3$) δ 1.90 (br, 1H), 2.82 (d, J = 6.2 Hz, 2H), 3.75 (br, 2H), 7.22–7.28 (m, 3H), 7.64–7.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.3, 37.8, 61.2, 111.8, 112.6, 127.8, 129.6, 135.1; IR (neat) 3368, 2159, 1573 cm^{-1}; elemental analysis calcd for $C_{10}H_{10}OTe$ (273.79): C, 43.87; H, 3.68; found: C, 43.83; H, 3.82.

1-(Phenyltelluro)-3-dimethylamino propyne (Table 4, entry 7): m.p. 64.0–64.8 ºC; ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 6H), 3.58 (s, 2H), 7.22–7.27 (m, 3H), 7.67–7.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 41.3, 44.0, 49.7, 110.5, 112.7, 127.7, 129.6, 135.0; IR ($CHCl_3$) 3019, 2400, 1574, 1574, 1475 cm^{-1}; elemental analysis calcd for $C_{11}H_{13}NTe$ (286.83): C, 46.06; H, 4.57; found: C, 45.84; H, 4.69.

1-[(Phenyltelluro)ethynyl] cyclohexene (Table 4, entry 8): ^{1}H NMR ($CDCl_3$) δ 1.52–1.68 (m, 4H), 2.12–2.20 (m, 4H), 6.14–6.16 (m, 1H), 7.17–7.27 (m, 3H), 7.63–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4, 22.2, 25.5, 29.2, 43.2, 113.5, 116.5, 121.2, 127.6, 129.6, 134.6, 137.9; IR (neat) 3051, 2928, 1573, 1474, 1434 cm^{-1}; elemental analysis calcd for $C_{14}H_{14}Te$ (309.86): C, 54.27; H, 4.55; found: C, 54.03; H, 4.64.

1-(Phenyltelluro)-2-(tri-isopropylsilyl) ethyne (Table 4, entry 9): ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 21H), 7.23–7.25 (m, 3H), 7.65–7.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 11.4, 18.5, 64.7, 113.1, 121.4, 127.5, 129.5, 134.4; IR (neat) 2942, 2864, 2073, 1574, 1462 cm^{-1}; elemental analysis calcd for $C_{17}H_{26}TeSi$ (386.08): C, 52.89; H, 6.79; found: C, 52.97; H, 7.00.

1-(Phenylthio)-2-(ethyl carboxylate) ethyne (Table 4, entry 10): ^{1}H NMR ($CDCl_3$) δ 1.29 (t, J = 7.1 Hz, 3H), 4.24 (dd, J = 7.1 and 14.2 Hz, 2H), 7.25–7.34 (m, 3H), 7.72–7.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 61.9, 77.2, 107.3, 110.8, 128.8, 130.0, 136.4, 152.1; IR (neat) 3019, 2137, 1700 cm^{-1}; elemental analysis calcd for $C_{11}H_{10}O_2Te$ (301.80): C, 43.78; H, 3.34; found: C, 43.53; H, 3.54.

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